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TWO-STEP MECHANISM FOR ORDER-DISORDER KINETICS IN SILICATES

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ABSTRACT

It is proposed that the apparent high activation energy barrier associated with the lower temperature limit T_{Tr} of cation ordering in certain silicates is attributable to a mechanism involving two consecutive steps in the ordering process. This mechanism is regarded as responsible for certain ordering characteristics which distinguish metamorphic, igneous plutonic and volcanic pyroxenes. An important consequence is that order-disorder equilibrium can be attained at temperatures below T_{Tr} only through recrystallization and not by thermal annealing which does not result in recrystallization.

CONTENTS

	Page
ABSTRACT	iii
INTRODUCTION.....	1
MECHANISM OF CONSECUTIVE STEPS	2
EXCLUSION OF THE COMPETING MECHANISM	6
NATURE OF THE LOW TEMPERATURE PROCESS.....	7
GEOLOGICAL CONSEQUENCES	7
ACKNOWLEDGMENTS	9
REFERENCES	10

ILLUSTRATIONS

Figure		Page
1	Potential energy diagrams for an intracrystalline exchange process involving species A and B between sites 1 and 2. The shapes of the wells and barrier have no significance.	12
2	Potential energy diagram for the inferred consecutive two-step exchange process. The L-energy barrier is assumed to be in control at low temperatures while the H-barrier is assumed to be in control at high temperatures. The latter barrier also corresponds to that of Fig. 1.	13
3	Suggested relation between the rate factors $K\phi$ of the high and low temperature steps of the two consecutive step mechanism and the temperature. The full lines indicate the temperature ranges in which the rate factors govern the over-all rate.	14

ILLUSTRATIONS (Continued)

Figure		Page
4	Required relation between the rate factor for two competing mechanisms. Full lines indicate temperature ranges in which the rate factors govern the observed rate.	15
5	Scheme illustrating the possibility of crystals attaining and retaining equilibrium distributions. The full lines indicate temperature ranges for different materials in which such distributions are readily attained and retained. Dashed lines indicate temperature ranges in which these possibilities are greatly diminished.	16

TWO-STEP MECHANISM FOR ORDER-DISORDER KINETICS IN SILICATES

INTRODUCTION

The kinetics of ionic intracrystalline exchange (order-disorder phenomena) is an important aspect of the thermal behavior of minerals. The recent experiments of Virgo and Hafner (1969) have indicated that the high temperature kinetics of order-disorder in orthopyroxene are consistent with a simple exchange model which had earlier been found applicable to metallic alloys (Dienes, 1955) and which has been adapted to silicates (Mueller, 1967). However Virgo and Hafner (1969) also made the important observation that there is an apparent cut-off or transition region on the temperature scale below which no more ordering or disordering occurs. They attributed this behavior to an unmeasured energy barrier different from the one which is operative above the cut-off temperature of approximately 480°C in orthopyroxene and which has a measured activation energy of about 20 kilocalories in the direction of disordering.

It is apparent that the postulated energy barrier which is operative below the cut-off range is sufficiently high to prevent ordering even on a geological time scale since natural pyroxenes of slowly cooled metamorphic rocks still possess considerable disorder (Ghose, 1964). As was pointed out by Virgo and Hafner the 20 kilocalory barrier is not sufficiently high to prevent such ordering and cannot account for the relatively narrow cut-off temperature region. Further

since natural cummingtonites from metamorphic rocks also show considerable disorder (Ghose, 1961), it is likely that a similar cut-off or transition in mechanisms applies in this case and other cases also. It is obvious however that the transition temperature T_{Tr} need not be the same in all silicates.

MECHANISM OF CONSECUTIVE STEPS

Two alternatives suggest themselves for the change of kinetic mechanisms which appears to be required to explain the ordering cut-off temperature T_{Tr} . These are (1) a two consecutive step mechanism involving a low temperature process with a high activation energy and a high temperature process with a lower activation energy, and (2) two competing processes. We shall adopt the first alternative and show later why the second alternative does not apply.

The exchange kinetics of species such as Mg^{2+} and Fe^{2+} in a quasi-binary crystal of the type of orthopyroxene may be represented by the following second order rate equation:

$$-\frac{dX_1}{dt} = \frac{1}{2} C_0 \left[K_{12} \phi_{12} X_1 (1 - X_2) - K_{21} \phi_{21} X_2 (1 - X_1) \right]. \quad (1)$$

In this equation X_1 and X_2 are the site occupancy fractions of either of the ionic species of a binary pair in the sites 1 and 2 respectively (represented in orthopyroxene by the symbols M_1 and M_2), K_{12} and K_{21} are the disordering and ordering rate constants, while ϕ_{12} and ϕ_{21} are corresponding factors analogous to activity coefficient products in macroscopic systems, except that they also

contain the thermodynamic properties of the activated state. C_0 is the total concentration (in moles or atoms cm^{-3}) of both sites 1 and 2. In the case of completely ideal solutions, including both the stable lattice sites and the activated state sites $\phi_{12} = \phi_{21} = 1$ and Eq. (1) reduces to its simplest form.

The potential energy relations which are reflected in the experimental activation energies and which are the chief contributors to the temperature sensitivity of the $K\phi$ factors may be represented as in Fig. 1. This figure in particular is intended to refer to the exchange process above the temperature T_{Tr} as manifested in such experiments as those of Virgo and Hafner (1969). In the latter case the experimental activation energies E_{ex12}^* and E_{ex21}^* which correspond to ΔU_{12}^* and ΔU_{21}^* for disordering and ordering were found to be

$$E_{ex12}^* = 20 \text{ kilocalories}$$

$$E_{ex21}^* = 16 \text{ kilocalories}$$

The cut-off temperature T_{Tr} can be best explained by resorting to two consecutive processes with potential energy configurations as depicted in Fig. 2. In this figure the high temperature (H) activated state corresponds to the 20 kilocalory barrier discovered in orthopyroxene by Virgo and Hafner while the low temperature (L) activated state corresponds to the barrier assumed to be operative below the cut-off temperature T_{Tr} . According to kinetic theory

(Glasstone, Laidler and Eyring, 1941) the system must pass over the highest barrier but need not pass through the intermediate state.

The mechanism of two consecutive reactions cannot however be explained solely on the basis of potential energy diagrams such as Fig. 2 or the corresponding experimental activation energies. Kinetic theory tells us that the absolute reaction rate constants K_{12} and K_{21} are determined by the Gibbs free energy of activation ΔG^* (Glasstone, Laidler and Eyring, 1941) since

$$K = \nu \frac{k T}{h} \exp (-\Delta G^*/RT) . \quad (2)$$

In this expression ν is the transmission coefficient, k is Boltzmann's constant, h is Planck's constant, and R is the gas constant. An additional relation is

$$\Delta G^* = \Delta H^* - T\Delta S^* , \quad (3)$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation respectively. In condensed systems such as this ΔG^* will not differ greatly from ΔF^* the Helmholtz free energy of activation and ΔH^* is consequently very similar to ΔE^* the internal energy of activation. Also these latter values should be similar in magnitude to the experimental activation energy E_{ex}^* .

The transmission coefficient in Eq. (2) is difficult to evaluate and in the absence of any evidence to the contrary is usually set equal to unity. However it is clear from Eqs. (2) and (3) that even if ΔH^* , ΔE^* and E_{ex}^* are small ΔG^* may be indeterminately large depending on T and ΔS^* , assuming that $\Delta S^* < 0$.

The possible effect of different values of ΔG^* and E_{ex}^* on the rate constants and their temperature sensitivities is depicted in Fig. 3. Since the initial state is the same for both high and low temperature processes and since the high temperature process appears to be governed by the simple second order rate Eq. (1), we may assume that the equation for the low temperature process has the same form and that only the values of the $K\phi$ factors of the two processes will differ throughout most of the temperature range. However it is postulated here that the $K\phi$ factors for the two processes have the same value at the cut-off temperature T_{Tr} .

In consecutive processes the over-all rate is governed by the step for which $K\phi$ has the lowest value. Consequently below T_{Tr} , $K_L\phi_L < K_H\phi_H$ while above this temperature $K_H\phi_H < K_L\phi_L$. We may also imagine another diagram analogous to Fig. 2 but with ΔG^* plotted instead of the potential energy. In such a diagram the height of the barrier would change drastically with the temperature so that in the high temperature range the H barrier would be higher than the L barrier. In this way it is possible to explain why at these temperatures only parameters such as E_{ex}^{*H} which refer to the high temperature process are registered. It is interesting that the negative value of the entropy of activation which is required for the high temperature process has been postulated on other grounds (Mueller, 1969).

Below the cut-off temperature where $K_L \phi_L$ is in control the temperature sensitivity of this rate constant is so great that it decreases rapidly to such low values that the exchange process is frozen even on the cooling time scale of metamorphic rocks. Thus it is possible that in a temperature interval of less than 100°K the value of K_L decreases some orders of magnitude. Although no data are as yet available for a quantitative calculation, it is possible to get a qualitative impression of the effect by substituting certain values of K_L and the temperature interval. Thus from the general relation

$$\frac{\partial \ln K_L}{\partial T} = \frac{E_{ex}^{*L}}{RT^2}, \quad (4)$$

where E_{ex}^{*L} is regarded as constant we obtain the integrated expression

$$\ln \frac{K_L''}{K_L'} = \frac{E_{ex}^{*L}}{R} \left(\frac{1}{T'} - \frac{1}{T''} \right), \quad (5)$$

where $K_L'' = K_H$ at $T'' = T_{Tr}$.

If for any temperature interval $\Delta T = T'' - T' = 100^\circ\text{K}$ and $T'' = T_{Tr} = 753^\circ\text{K}$ (480°C), and if we take $(K_L''/K_L') = 10^6$ we find that $E_{ex}^{*L} \approx 140,000$ calories. It is obvious that in a smaller temperature interval or for a larger change in K_L E_{ex}^{*L} would be even larger.

EXCLUSION OF THE COMPETING MECHANISM

In a mechanism involving competing processes the governing process of the over-all rate is that which occurs most rapidly. This situation is depicted

in Fig. 4, which is a schematic drawing analogous to Fig. 3. It is clear from this figure however that a mechanism involving competing processes is incapable of explaining the observations in any simple way since the low temperature process involves a less steep slope below T_{Tr} than that of the high temperature process. Consequently it is impossible for a great decrease in ordering (and disordering) rates to occur below T_{Tr} .

NATURE OF THE LOW TEMPERATURE PROCESS

So far we have merely interpreted the observed ordering cut-off temperature as resulting from a two step mechanism without identifying the atomistic behavior responsible. Because of the inferred high activation energy for the low temperature process it seems likely that bond breaking is involved. Perhaps also this process involves the activation of vacancies which are inferred to play an important role in particle migration in crystal lattices (Dienes and Damask, 1965). Unfortunately it is impossible to characterize the kinetics in any greater detail than this now and it is likely that this will be possible only after extensive experimental work in the temperature range of T_{Tr} .

GEOLOGICAL CONSEQUENCES

Some consequences of the experimentally determined kinetic behavior of orthopyroxene have already been pointed out by Virgo and Hafner (1969), but others come to our attention by considering the theoretical model. The general behavior of such silicates may best be summarized by a schematic diagram

such as that of Fig. 5. This figure illustrates the extent of attainment of heterogeneous and homogeneous equilibrium in the variety of environments encountered in natural samples.

It is clear first of all from Fig. 5 that the macroscopic intercrystalline exchange equilibrium (line a) may in principle be attained and quenched in at any temperature at which crystallization or recrystallization can occur and merely reflects the latest of such events. However the establishment of this equilibrium requires the extensive reconstruction of the crystals involved except when unmixing occurs on dimension scales of some tens of microns as a maximum (Mueller, 1969). For example an intercrystalline distribution established at solidus temperatures in a plutonic igneous rock can only be destroyed by recrystallization at a lower temperature such as might be induced by shearing stresses. On the other hand the corresponding intracrystalline exchange equilibria of such rocks (line b) will not ordinarily be quenched in at any temperature because of the slow cooling rate. The same conclusion also applies to metamorphic rocks (line c) above the temperature T_{Tr} . However in these rocks the attainment of the intracrystalline equilibria is possible below T_{Tr} if crystallization or recrystallization occurs at these temperatures. The basis for this conclusion is that the establishment of the intracrystalline distributions should generally occur more readily than those between crystals (Mueller, 1969).

There is of course a slight probability that some igneous plutonic and metamorphic silicates could have their intracrystalline distributions quenched in

above the temperature T_{Tr} , as is indicated by the dashed lines. This could occur for example if a recrystallizing metamorphic rock were cooled rapidly by introduced water along a fracture.

Only in volcanic rocks however is there a high probability for quenching of the intracrystalline distributions and such distributions were indeed measured by Ghose and Hafner (1967). This characteristic is indicated by line d in Fig. 5.

The lower segment of line c is particularly interesting because it indicates that if a slowly cooled crystal such as a metamorphic orthopyroxene crystallized or recrystallized above T_{Tr} the observed distribution of Mg^{2+} and Fe^{2+} between the M sites all approximate the equilibrium distribution at T_{Tr} except that T_{Tr} itself is likely to vary somewhat as a function of compositional details. Thus it is unlikely that a suite of metamorphic orthopyroxenes define an equilibrium isotherm in detail.

ACKNOWLEDGMENTS

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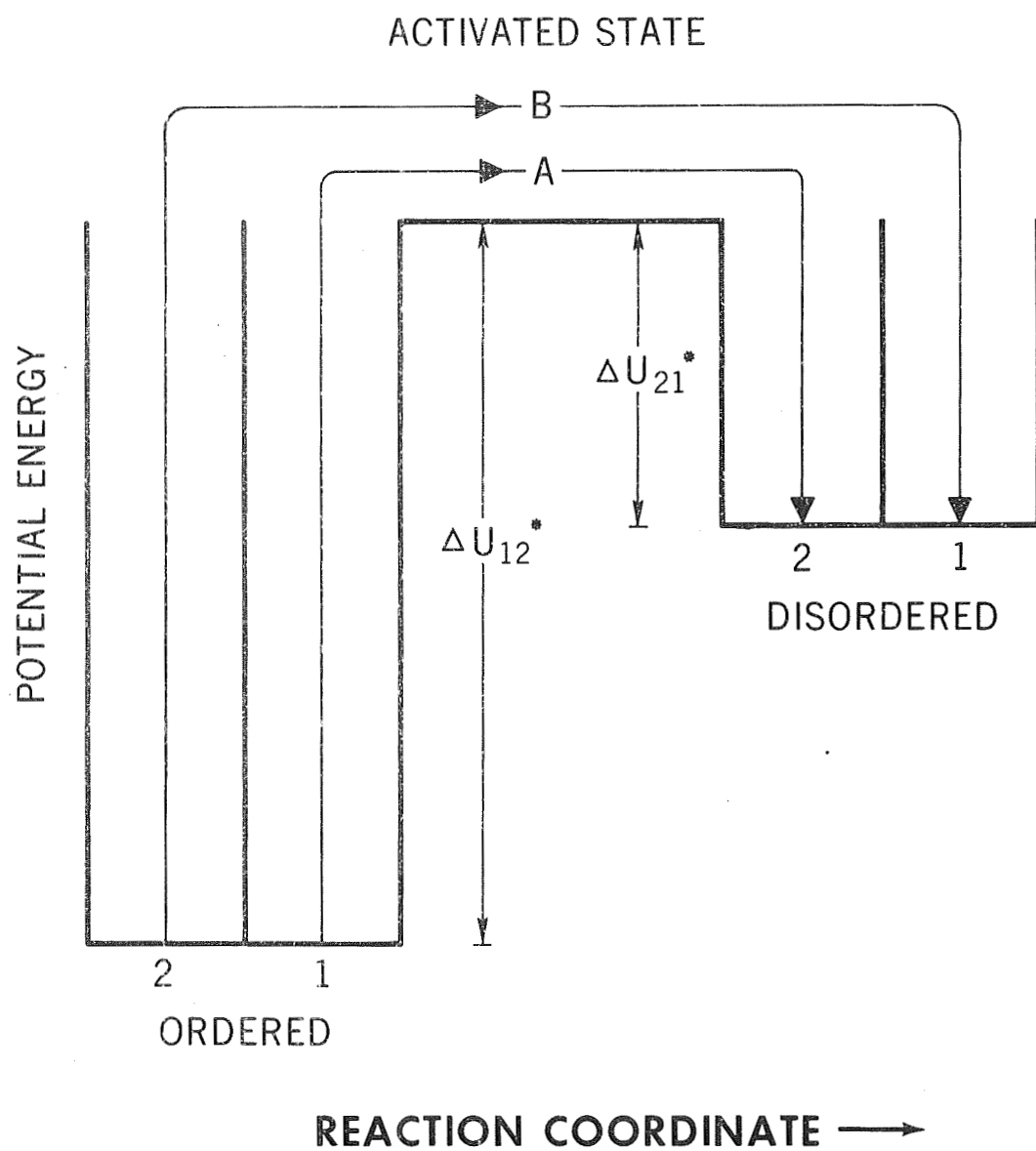


Figure 1. Potential energy diagrams for an intracrystalline exchange process involving species A and B between sites 1 and 2. The shapes of the wells and barrier have no significance.

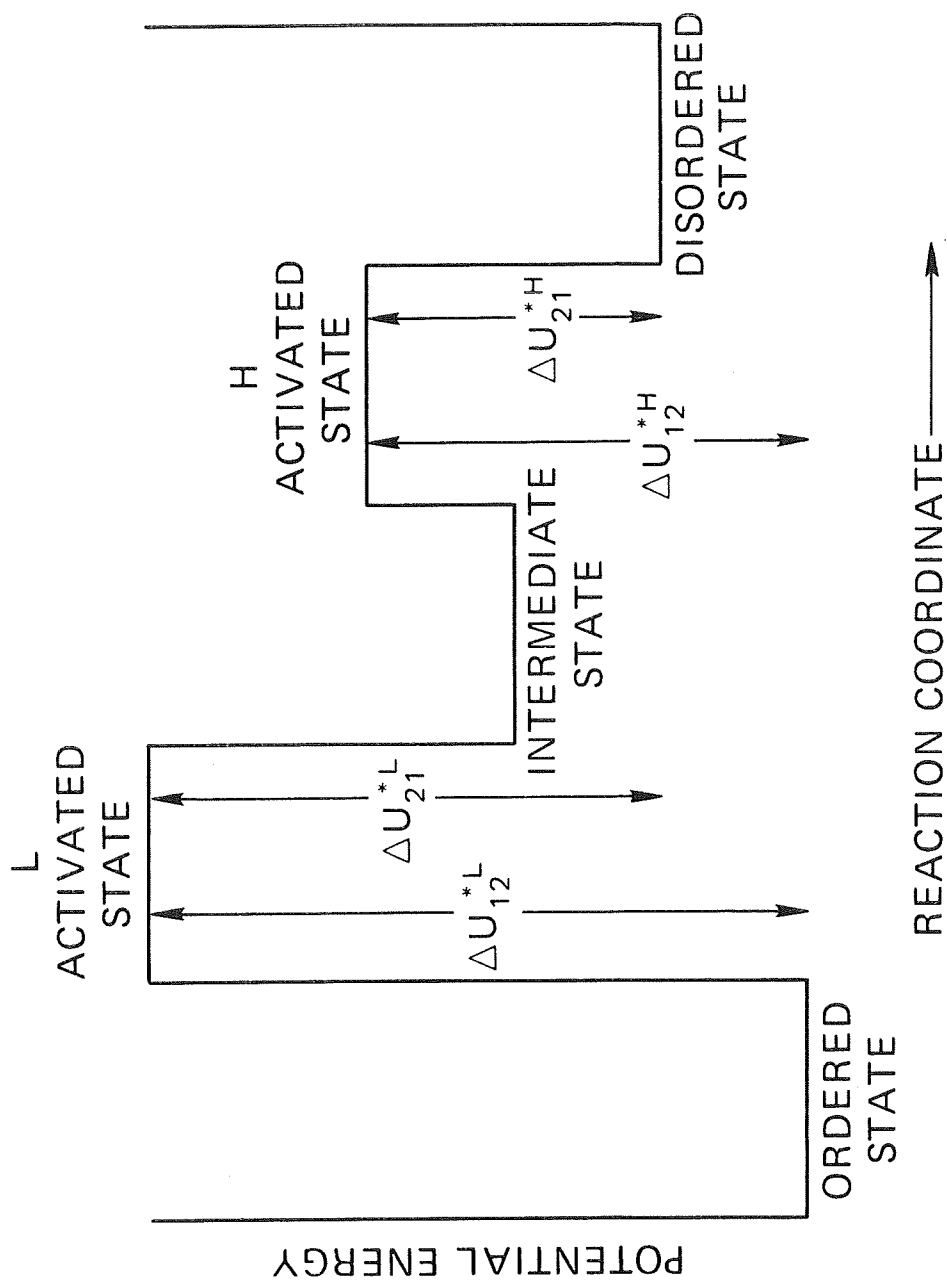


Figure 2. Potential energy diagram for the inferred consecutive two-step exchange process. The L-energy barrier is assumed to be in control at low temperatures while the H-barrier is assumed to be in control at high temperatures. The latter barrier also corresponds to that of Fig. 1.

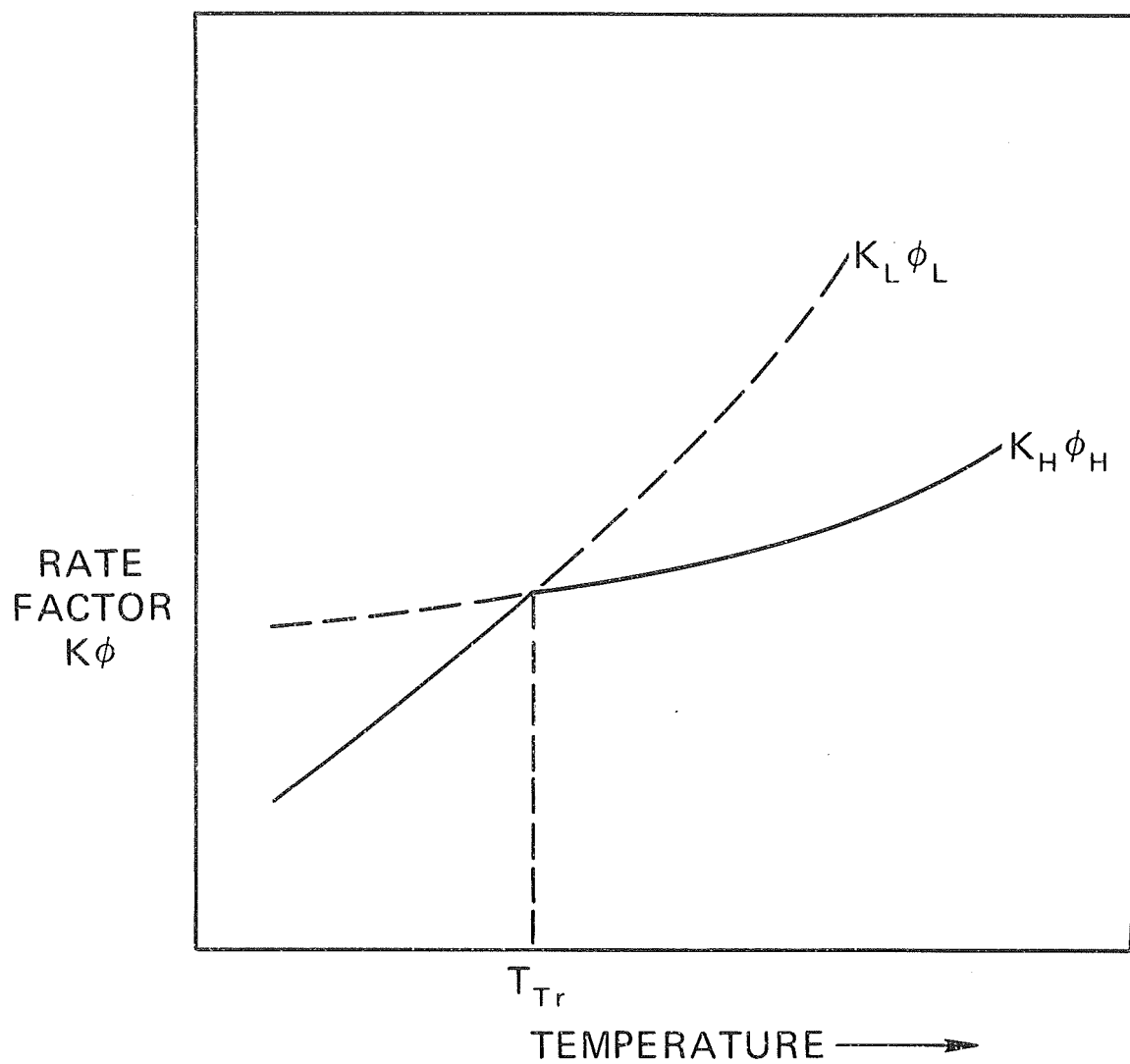


Figure 3. Suggested relation between the rate factors $K\phi$ of the high and low temperature steps of the two consecutive step mechanism and the temperature. The full lines indicate the temperature ranges in which the rate factors govern the over-all rate.

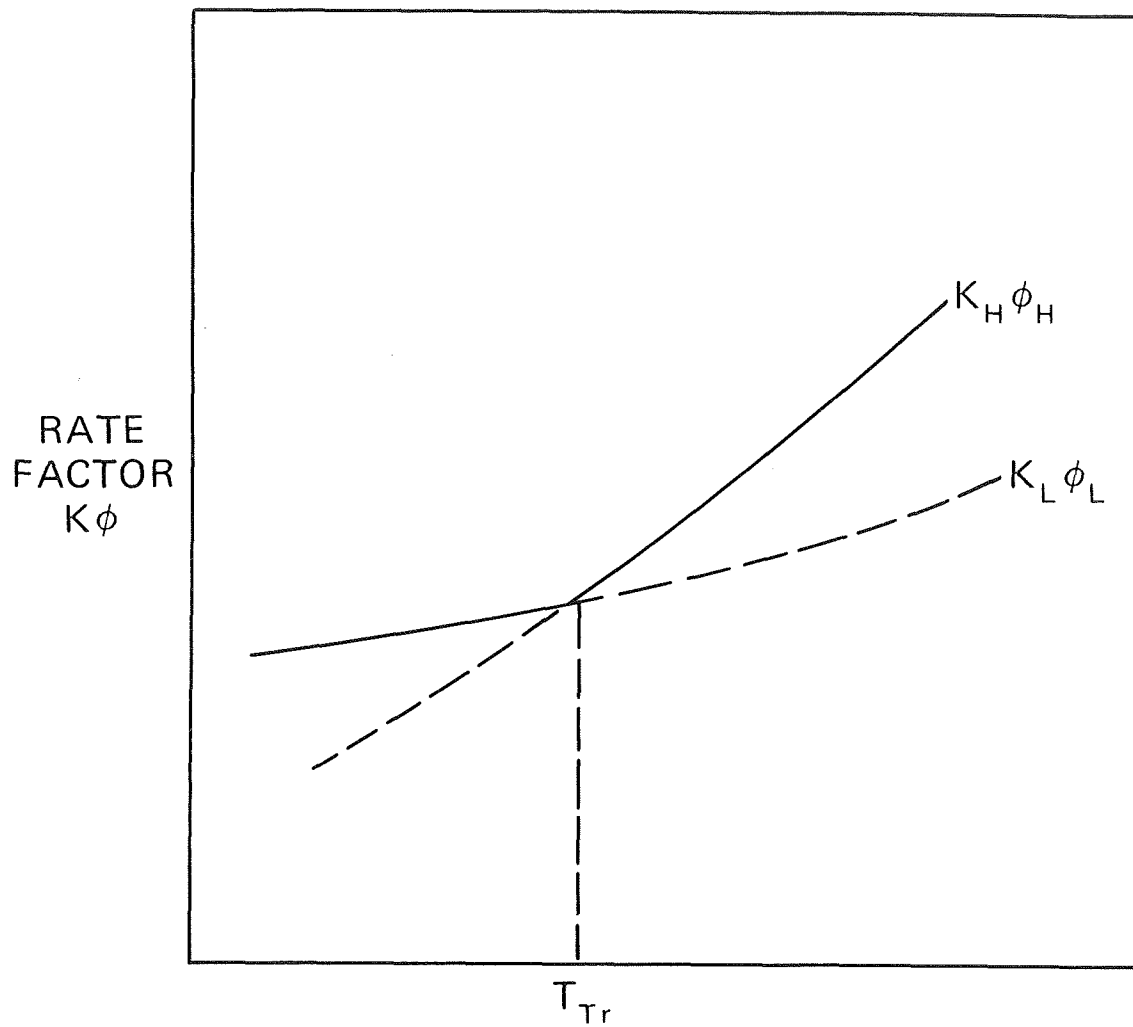


Figure 4. Required relation between the rate factor for two competing mechanisms. Full lines indicate temperature ranges in which the rate factors govern the observed rate.

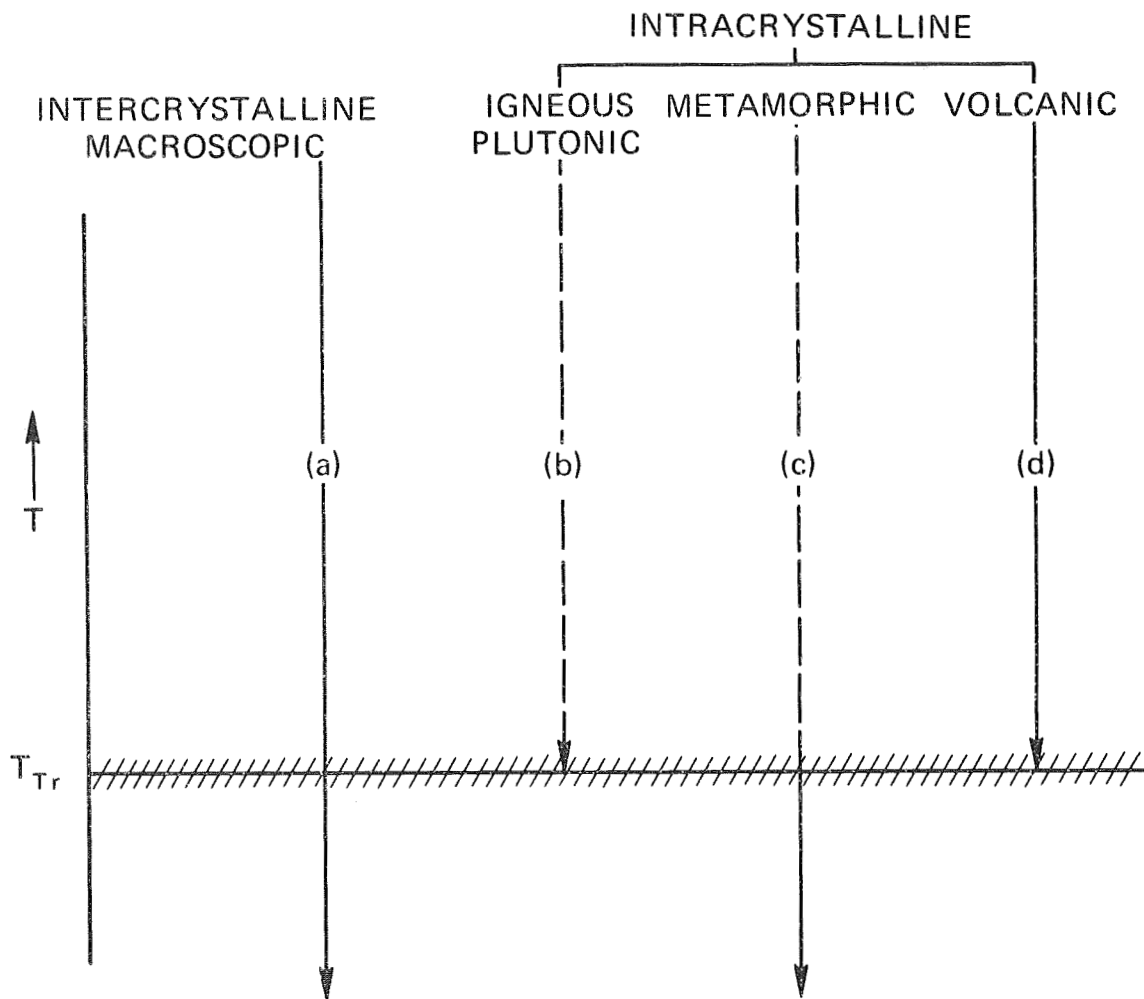


Figure 5. Scheme illustrating the possibility of crystals attaining and retaining equilibrium distributions. The full lines indicate temperature ranges for different materials in which such distributions are readily attained and retained. Dashed lines indicate temperature ranges in which these possibilities are greatly diminished.